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PHOTOASSISTED REACTION OF H<sub>2</sub> WITH CO<sub>2</sub> OVER SOLID  
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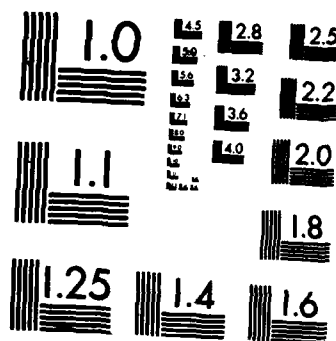
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Technical Report No. 1

Photoassisted Reaction of  $H_2$  with  $CO_2$   
over Solid Catalysts

by

Norman N. Lichtin, K.M. Vijayakumar and B.I. Rubio

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The dark and photoassisted reactions of  $\text{CO}_2$  with  $\text{H}_2$  over  $\alpha\text{-Fe}_2\text{O}_3$ , Zn-Fe-Oxide, Co-Mo-Al-oxide, Co-Mo-Ti-oxide, platinized La-Ni-oxide and platinized  $\text{SrTiO}_3$  have been investigated in the absence and presence of water vapor. Illumination was by a Hg-Xe-lamp at wavelengths above 350nm. The incident light flux, measured by ferrioxalate actinometry, was  $(1.02 \pm 0.08) \times 10^{17}$  photons/sec. Reactants in the ratio of  $\text{H}_2:\text{CO}_2 = 2:1$  were passed once over dry films of powdered catalysts at  $30^\circ\text{C}$  and 1 atm with contact times of 1/2 or 1 min. Products were analyzed by gas chromatography. No reaction took place in the absence of catalyst. Catalyzed rates of production of products were constant over the 22hr periods investigated. CO was the only product obtained in significant amounts in the dark. Under illumination, rates of formation of CO increased by a factor of 2 - 4.5.  $\text{CH}_4$  was the only other product of the photoassisted reaction in the absence of water vapor, with yields less than 0.2mole% of those of CO. In the presence of water vapor (3 mole% of supplied  $\text{CO}_2$ ), formic acid was produced at rates up to 19mole% the rate of formation of CO, along with minor amounts of  $\text{CH}_4$ ,  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{OH}$ , all produced at rates less than 0.2mole% that of CO. The highest photoassisted yields were obtained over Co-Mo-Al oxide, with efficiency of conversion of incident photons into products around 0.35molecule of product/incident photon. The corresponding estimated quantum yield was 1 molecule of product/absorbed photon. Over this catalyst, in the presence of water vapor and under the arbitrary conditions employed, the observed fractional conversion of  $\text{CO}_2$  to products was about ten times the value for gas-phase equilibrium calculated from thermodynamic data.

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PHOTOASSISTED REDUCTION OF  $\text{CO}_2$  BY  $\text{H}_2$  OVER METAL OXIDES IN  
THE ABSENCE AND PRESENCE OF WATER VAPOR

by

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## 1. INTRODUCTION

We have previously reported initial results of an investigation of the photoassisted reduction of  $\text{CO}_2$  by  $\text{H}_2$  over  $\alpha\text{-Fe}_2\text{O}_3$ , Zn-Fe-oxide, platinized La-Ni-oxide, Co-Mo-Al-oxide and Co-Mo-Ti-oxide in the absence and presence of water<sup>1</sup>. We now report more extensive quantitative yield data for the same reactant systems with the same catalysts, as well as with platinized  $\text{SrTiO}_3$ , and the relationship of yields to incident and absorbed light energy. The data are compared with calculated gas phase equilibrium compositions and it is shown that, with the most active catalyst, Co-Mo-Al-oxide, photoassisted consumption of  $\text{CO}_2$  in the presence of water vapor under arbitrarily chosen conditions was about 10 times greater than would be expected from gas-phase equilibration. Over this catalyst, the observed efficiency of use of incident photons was 0.35 molec. of photoproduct per incident photon, corresponding to an estimated quantum yield of 1 molec. of photoproduct per photon absorbed by the catalyst.

## 2. MATERIALS AND METHODS

**2.1 Catalysts and Reactants** Preparations of the previously reported catalysts and the sources and grades of the reagents used in these preparations and of

H<sub>2</sub>, Ar and CO<sub>2</sub> were as described previously.<sup>1</sup> High-purity He was supplied by Linde and Co. Pfaltz and Bauer research grade SrTiO<sub>3</sub> was platinized by treatment with 0.1wt% aqueous chloroplatinic acid and dried in Ar at 200°C. As previously reported, the atomic ratio of Zn to Fe in Zn-Fe-oxide was 1:2 and that of La to Ni in La-Ni-oxide was 1:1. The composition of Co-Mo-Al-oxide was 4.5wt% CoO, 15wt% MoO<sub>3</sub> and 80.5wt% Al<sub>2</sub>O<sub>3</sub> while that of Co-Mo-Ti-oxide was 3.5wt% CoO, 10wt% MoO<sub>3</sub> and 86.5wt% TiO<sub>2</sub>.

**2.2 Catalyst Films** Procedures for preparation of films were essentially as previously reported<sup>1</sup> except that He was used in place of N<sub>2</sub> for preconditioning films.

**2.3 Reaction Apparatus** Reactions were performed in 5x5x1cm or 4x7x2cm flow-through cells with flat major faces. A cell was connected to a gas flow system which provided reactants and carried the gas stream beyond the cell to a sampling valve coupled to the analytical system. The reaction cell was immersed in a water-bath thermostatted to  $\pm 0.05^\circ\text{C}$ . Illumination was by a 200W Schoeffel Hg-Xe lamp equipped with a collimating lens system and mounted on an optical bench at a distance of 45cm from the cell. Short-wavelength ultraviolet and long-wavelength infrared were eliminated by, respectively, a 350nm Corning cut-off filter and the water bath. The light beam was split and the relative intensity of the light flux incident on the cell was continuously monitored with a #4382 Pacific Instruments photomultiplier connected to a recorder.

**2.4 Reaction Conditions and Analyses of Products** Reactions at the gas-solid interface were carried out at 1atm and 29.8°C by passing 59-64 mL/min of a mixture of H<sub>2</sub> and CO<sub>2</sub> at a molar ratio of, respectively, 1.85-2.13 to 1 for 3 to 22 hr. Condensable products were trapped in 10-20mL of water maintained at

0°C. Water vapor, when present, was at a molar ratio of 0.03 to 1 relative to CO<sub>2</sub>. Collection of condensible products and sampling of the reacted gas stream were started 30min after reaction was begun. Products were analyzed with a Perkin Elmer Sigma 300 gas chromatograph equipped with gas-sampling and column-switching valves, thermal conductivity and flame ionization detectors in series, and a Perkin Elmer LCI-100 computing integrator. Products trapped in water were analyzed on a Porapak-N column while products sampled from the gas stream downstream from the ice-trap were analyzed on Porapak-N and MS-5A columns, used in series with column switching. Formation of formic acid was confirmed spectrophotometrically<sup>2</sup> using a Cary 210 instrument. Formaldehyde was determined by the chromotropic acid method<sup>3</sup>. Production of CO was qualitatively confirmed by the NBS Pd-silicomolybdate method<sup>4</sup>.

**2.5 Actinometry** The incident light flux was measured by ferrioxalate actinometry<sup>5</sup> and the resulting data was used to calibrate the on-line photometer. Potassium oxalate monohydrate was Baker Analyzed Reagent, ferric chloride hexahydrate and sodium acetate trihydrate were both Fisher ACS Reagent grade, and phenanthroline monohydrate was Smith ACS Reagent grade. A 350-480nm band-pass filter was used in optical series with a 350nm cut-off filter to isolate the lamp flux at 350-480nm. The only significant components of the Hg-Xe lamp emission at 350-480nm are the mercury bands at 366, 405 and 436nm. In addition, the filters passed some light at wavelengths above 700nm. The total flux from the lamp which was incident on the cell was calculated from the actinometric data, the known characteristics of the filters and the known emission spectrum of the lamp. Four replicate measurements gave a value for the total lamp flux from 350-1000nm of  $(1.02 \pm 0.08) \times 10^{17}$  quanta/sec. The uncertainties in calculating the total flux from the actinometric data are



probably greater than the quoted standard deviation which was calculated from the experimental reproducibility. Based on the above value of the flux and the illuminated area of the cell,  $7.1\text{cm}^2$ , the spatially averaged flux was  $1.4 \times 10^{16}$  quanta/sec- $\text{cm}^2$ . Fluctuations calculated from variations in photometer readings were negligible.

### 3. RESULTS

3.1 Products from Reaction of  $\text{CO}_2$  with  $\text{H}_2$  in the Absence of Water Vapor No products were detectable from reaction in the dark or under illumination in the absence of any catalyst. Yields of products formed in the presence of catalysts are summarized in Table 1. CO was the major product formed over all the catalysts and  $\text{CH}_4$  was the principal minor product. Formic acid was not detectable in the absence of water vapor. All the catalysts which were investigated promoted reduction in the dark. Yields increased by a factor of 2-4.5 upon illumination of catalyst films, demonstrating that photoassisted reaction occurs with all the catalysts. Yields of CO were measured after both 3hr and 20-22hr of illumination. With all the catalysts, the average rate of production of CO, i.e., the total yield divided by the period of illumination, was independent of the period of illumination, indicating that catalytic activity remained constant for at least 20-22hr.

3.2 Products from Reaction of  $\text{CO}_2$  and  $\text{H}_2$  in the Presence of Water Vapor No product was detectable in the dark or under illumination in the absence of any catalyst. Results obtained in the presence of water vapor, summarized in Table 1, were independent of whether the reaction time was 3hr or 20-22hr. The presence of water vapor had little effect on dark yields of CO except over Co-Mo-Ti-oxide, where a 14% decrease was observed. Methane, in trace amounts, was the only product other than CO which was detected in the dark reaction.

Under illumination, yields of formic acid corresponding to 6.6-19mole% of the yields of CO were obtained. With all the catalysts except one, the sum of the yields of formic acid and CO obtained under illumination differed by only 0.04-4.5mole% from the yield of CO obtained under illumination in the absence of water vapor. With platinized La-Ni-oxide, the sum of the yields of these two products corresponded to 21mole% more than the yield of CO in the absence of water vapor. Minor products which were also observed in the photoassisted reaction in the presence of water vapor included  $\text{CH}_4$  corresponding to 0.2mole% or less of the yields of CO,  $\text{CH}_3\text{OH}$  corresponding to 0.01mole% or less of the yields of CO, and traces of formaldehyde.

3.3 Efficiencies of Chemical Use of Incident and Absorbed Photons The determination of the magnitude of the incident light flux is described in section 2.5, above. It is assumed here that the absolute error in the flux is no larger than  $0.3 \times 10^{17}$  quanta/sec. The estimated error in yields of products and their average rate of production is  $\pm 5\%$ , or less. Thus, it is assumed that efficiencies of use of incident photons given in this paper have a reliability of about  $\pm 35\%$ . Values of efficiencies of use of incident photons,  $E_i = (\text{molec. of photo-prod./sec})/(\text{quanta incident/sec})$ , calculated from the data of Table 1, are given in Table 2. Rates of formation of photo-products were obtained by subtracting rates of the dark reaction from corresponding rates under illumination.

For each of the six catalysts, values of  $E_i$  in the presence and absence of water vapor are similar. Over the entire range of the experiments,  $E_i$  varies from .06 (with Co-Mo-Ti-oxide in the presence of water vapor) to 0.37 (with Co-Mo-Al-oxide in the presence of water vapor). Although the absolute values of  $E_i$  are estimated to be uncertain to around  $\pm 35\%$ , only the uncertainty in product yields, i.e.,  $\pm 5\%$ , is pertinent to their relative values.

An additional source of uncertainty enters into the estimate of quantum efficiencies,  $E_q = (\text{molec. of photo-product/sec})/(\text{quanta absorbed/sec})$ . Rather than measuring the rate of absorption of photons by the catalysts, it has been assumed that all incident photons with energies equal to or greater than the band-gap of a given semiconductor were absorbed. The corresponding values of absorbed photon flux were then calculated from the measured incident flux with the aid of the emission spectrum of the Hg-Xe lamp. Literature values<sup>6</sup> of the band gaps of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{SrTiO}_3$  were estimated to correspond to absorption of, respectively, 64% (2.2eV) and 25% (3.2eV) of the incident photon flux. The literature value<sup>6</sup> of the band-gap of  $\text{MoO}_3$  (2.9eV) was used to estimate the fraction of incident light absorbed by the two cobalt-containing oxides as 36%. La-Ni-oxide, a narrow-band electronic conductor<sup>7</sup>, is assumed to absorb the entire incident photon flux. No data on the band-gap of Zn-Fe-oxide appears to be available. Values of  $E_q$  are presented in Table 3. It is noteworthy that the highest values of  $E_q$ , obtained with Co-Mo-Al-oxide in the presence and absence of water vapor, are indistinguishable from unity.

#### 4. DISCUSSION

**4.1 Evidence of Catalytic Action** The probability of the metal oxides used in this research functioning as significant sources of reducing equivalents is small. With two exceptions, metallic Pt and Co(II), all the metals were present in their highest common oxidation states, namely, Fe(III), Zn(II), Mo(VI), Al(III), Ti(IV), La(III), Ni(II) and Sr(II). The possibility that either Pt, Co(II) or impurities were significant reactants can be evaluated from the number of reducing equivalents required to produce the observed yields. E.g., 5.9mmole of CO and formic acid were produced in 22hr of

photoassisted reaction over Co-Mo-Al-oxide in the presence of water vapor, corresponding to 11.8 millireducing equivalents. Assuming 200mg of catalyst (see section 2.2), the 4.5wt% of CoO present in it corresponded to only 0.12 millireducing equivalents. Similarly, the 4.6meq of reduced products obtained in 21hr of photoassisted reaction over  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the presence of water vapor can be compared with the 1.25mmole of the catalyst present in 200mg of this compound. Similar consideration of the data for all the catalysts demonstrates that in no case could a substantial part of the observed products have resulted from reaction with catalyst or impurity.

4.2 Consumption of H<sub>2</sub> Data on consumption of H<sub>2</sub>, which is summarized in Table 3, is based on yields of CO and HCO<sub>2</sub>H, measured flow-rates of H<sub>2</sub> and the assumption that only CO and H<sub>2</sub>O or HCO<sub>2</sub>H were produced in the reaction. Utilization of H<sub>2</sub> appears to be inefficient. However, no effort was made to optimize it by, e.g., recirculating it in a closed system.

4.3 Implication of Estimated Quantum Yields The highest values of  $E_q$  recorded in Table 3 are 1.0 for Co-Mo-Al-oxide and 0.7 for TiO<sub>2</sub>. If it is assumed that both these values reflect conversion efficiencies which differ little from unity, they can provide some insight into the photoassisted process. The units of  $E_q$  are molecules of product produced per absorbed photon. However, CO<sub>2</sub> is actually reduced by 2 reducing equivalents. An electron-transfer mechanism in which one photon promotes transfer of two electrons is not plausible. More probable are mechanisms in which absorption of a photon by the catalyst results in activation of a sorbed molecule so that it then undergoes reaction. Photoactivation of sorbed CO<sub>2</sub> in this fashion is an example of such a process. A practical implication of the observed values of  $E_q$  is the possibility that, if quantum yields are independent of light

intensity at substantially higher intensities, proportionally higher rates of reaction can be obtained.

4.4 Relationship between Photoassisted Yields in the Presence and Absence of Water The fact that photoassisted yields of CO in the absence of water differ little from the sum of photoassisted yields of CO plus  $\text{HCO}_2\text{H}$  in the presence of water supports the conclusion that the principal effect of water is to divert part of the photoassisted reaction from production of CO to production of formic acid. However, the data provide no mechanistic inferences and do not provide a basis for concluding whether CO is a precursor of formic acid.

4.5 Comparison of Equilibrium Conversion with Photoassisted Conversion The reaction which produces CO is presumably the reverse of the water-gas shift reaction. Observed efficiencies for the conversion of  $\text{CO}_2$  can be compared with fractional conversions calculated from thermodynamic data for the gas-phase water-gas shift reaction<sup>8</sup>. The equilibrium constant calculated for the formation of CO is  $1.23 \times 10^{-5}$  at  $30^\circ\text{C}$ . Percent conversions of  $\text{CO}_2$ , calculated from this value, are compared in Table 3 with conversion efficiencies obtained with the most active catalyst employed, Co-Mo-Al-oxide. No effort was made to establish equilibrium in the dark reaction or to achieve the photostationary state under illumination. Nevertheless, the fact that photoassisted conversion efficiency exceeds the value calculated for gas-phase equilibrium, and by a factor of about 10 in the presence of added water vapor, suggests that there is a large difference between the dark equilibrium and photostationary states and supports the possibility of obtaining substantially higher efficiencies of conversion of  $\text{CO}_2$  and  $\text{H}_2$  by manipulation of conditions, e.g., residence time of reactants in the cell and intensity of illumination and area of catalyst surface accessible to light.

## ACKNOWLEDGMENT

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TABLE 1  
Average Rates of Production of Products in  
the Reaction of Flowing<sup>a</sup> CO<sub>2</sub> and H<sub>2</sub> over Films of Metal Oxides<sup>b</sup>  
at 1 Atm<sup>c</sup> and 29.8°C

Catalyst	Photo-assisted	Average Rate of Production in the absence of (H <sub>2</sub> O)g $\mu$ mole/hr		Average Rate of Production in presence of (H <sub>2</sub> O)g $\mu$ mole/hr				
		CO	CH <sub>4</sub>	CO	CH <sub>4</sub>	HCO <sub>2</sub> H	CH <sub>2</sub> O	CH <sub>3</sub> OH
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	No	58	----	54	----	----	----	----
	Yes	116	----	102	0.11	8.9	Tr	0.10
Zn-Fe-oxide	No	110	----	114	Tr	----	----	----
	Yes	234	0.29	215	0.36	20.1	Tr	0.11
Co-Mo-Al-oxide	No	64	----	59	Tr	----	----	----
	Yes	280	0.41	267	0.41	19.3	Tr	0.21
Co-Mo-Ti-oxide	No	88	----	102	----	----	----	----
	Yes	138	0.12	126	Tr	14.8	Tr	0.07
Pt-La-Ni-oxide	No	102	----	108	----	----	----	----
	Yes	158	0.21	160	0.22	30.8	Tr	0.15
Pt-SrTiO <sub>3</sub>	No	64	----	59	----	----	----	----
	Yes	172	0.32	160	0.31	10.6	Tr	0.06

a. 16-17 mmole/hr

b. 0.15-0.20 g. of finely ground catalyst in 25 or 28cm<sup>2</sup> films;

c. Partial pressures: CO<sub>2</sub>, 0.33  $\pm$  0.02 atm; H<sub>2</sub>, 0.67  $\pm$  0.04 atm; H<sub>2</sub>O when present, 0.01 atm.

TABLE 2

Efficiencies<sup>a</sup> of Utilization of H<sub>2</sub> and Photons in the Reaction of CO<sub>2</sub> with H<sub>2</sub> over Metal Oxides in the Absence and Presence of Water Vapor<sup>b</sup>

Catalyst	Water Vapor	Photo-assisted	Efficiencies of Use		
			H <sub>2</sub> %	Photons E <sub>i</sub>	Photons E <sub>q</sub>
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	No	No	0.06	----	----
	No	Yes	0.11	0.10	0.15
	Yes	No	0.05	----	----
	Yes	Yes	0.10	0.09	0.14
Zn-Fe-oxide	No	No	0.11	----	----
	No	Yes	0.24	0.20	----
	Yes	No	0.11	----	----
	Yes	Yes	0.24	0.20	----
Co-Mo-Al-oxide	No	No	0.07	----	----
	No	Yes	0.28	0.34	0.98
	Yes	No	0.07	----	----
	Yes	Yes	0.29	0.37	1.03
Co-Mo-Ti-oxide	No	No	0.09	----	----
	No	Yes	0.14	0.08	0.23
	Yes	No	0.10	----	----
	Yes	Yes	0.14	0.06	0.18
platinized La-Ni-oxide	No	No	0.10	----	----
	No	Yes	0.16	0.09	0.09
	Yes	No	0.11	----	----
	Yes	Yes	0.19	0.14	0.14
platinized SrTiO <sub>3</sub>	No	No	0.07	----	----
	No	Yes	0.17	0.18	0.71
	Yes	No	0.06	----	----
	Yes	Yes	0.17	0.18	0.73

a. Efficiencies in the presence of water vapor are based on sums of the yields of CO and HCO<sub>2</sub>H. Values of E<sub>i</sub> and E<sub>q</sub> are expressed in pure numbers, not in percent.

b. Conditions given in Table 1.



TABLE 3

Comparison of Observed Conversion of  $\text{CO}_2$  over Co-Mo-Al-oxide at  $30^\circ\text{C}$   
and 1min Residence Time with Gas-Phase Equilibrium Conversion<sup>a</sup>

Concentrations of Reactants			% Conversion		
$\text{CO}_2$	$\text{H}_2$	$\text{H}_2\text{O}$	Calculated Equilibrium	Observed Dark	Observed Photoassisted
11.9	28.1	----	0.54	0.15	0.65
13.2	27.0	0.54	0.06	0.12	0.60 <sup>b</sup>

a. Conditions given in Table 1.

b. Based on sum of yields of CO and  $\text{HC}_2\text{OH}$ .

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